

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: D01F 9/12, 9/127, C01B 31/02	A1	(11) International Publication Number: WO 99/06618 (43) International Publication Date: 11 February 1999 (11.02.99)
(21) International Application Number: PCT/US98/16071 (22) International Filing Date: 31 July 1998 (31.07.98) (30) Priority Data: 08/910,495 4 August 1997 (04.08.97) US (71) Applicant: HYPERION CATALYSIS INTERNATIONAL, INC. [US/US]; 38 Smith Place, Cambridge, MA 02138 (US). (72) Inventors: MOY, David; 21 Edward Drive, Winchester, MA 01839 (US). CHISHTI, Asif; 1251 Pawtucket Boulevard #1, Lowell, MA 01852 (US). (74) Agents: EVANS, Barry et al.; Whitman Breed Abbott & Morgan LLP, 200 Park Avenue, New York, NY 10166 (US).	(81) Designated States: AL, AM, AT, AU, AZ, BA, BE, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	
(54) Title: PROCESS FOR PRODUCING SINGLE WALL NANOTUBES USING UNSUPPORTED METAL CATALYSTS AND SINGLE WALL NANOTUBES (57) Abstract A process for producing hollow, single-walled carbon nanotubes by catalytic decomposition of one or more gaseous carbon compounds by first forming a gas phase mixture of carbon feed stock gas comprising one or more gaseous carbon compounds, each having one to six carbon atoms and only H, O, N, S or Cl as hetero atoms, optionally admixed with hydrogen, and a gas phase metal containing compound which is unstable under reaction conditions for said decomposition, and which forms a metal containing catalyst which acts as a decomposition catalyst under reaction conditions; and then conducting said decomposition reaction under decomposition reaction conditions, thereby producing said nanotubes.		

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

TITLE OF THE INVENTION

**PROCESS FOR PRODUCING SINGLE WALL NANOTUBES USING
UNSUPPORTED METAL CATALYSTS AND SINGLE WALL NANOTUBES**

5

BACKGROUND OF THE INVENTION**Field of the Invention**

This invention relates to a method for producing single wall carbon nanotubes, also known as
10 linear fullerenes, employing unsupported metal containing catalysts, for decomposition of a C₁ to C₆ carbon feedstock such as carbon monoxide.

Description of the Related Art**Multi-walled Carbon Nanotubes**

15 Multi-walled carbon nanotubes, or fibrils, are well-known. Typically, carbon fibrils have a core region comprising a series of graphitic layers of carbon.

Since the 1970's, carbon nanotubes and fibrils have been identified as materials of interest for a
20 variety of applications. Submicron graphitic fibrils belong to a class of materials sometimes called vapor grown carbon fibers. Carbon fibrils are vermicular carbon deposits having diameters less than approximately 1.0 μ . They exist in a variety of forms and have been
25 prepared through the catalytic decomposition of various carbon-containing gases at metal surfaces. Such vermicular carbon deposits have been observed almost since the advent of electron microscopy. A good early survey and reference is found in Baker and Harris,
30 Chemistry and Physics of Carbon, Walker and Thrower ed., Vol. 14, 1978, p. 83, and in Rodriguez, N., J. Mater. Research, Vol. 8, p. 3233 (1993).

Carbon fibrils were seen to originate from a metal catalyst particle which, in the presence of a
35 hydrocarbon containing gas, became supersaturated in carbon. A cylindrical ordered graphitic core is extruded which immediately became coated with an outer layer of

pyrolytically deposited graphite. These fibrils with a pyrolytic overcoat typically have diameters in excess of 0.1μ . (Obelm, A. and Endo, M., J. Crystal Growth, 32:335-349(1976).)

5 Tibbetts has described the formation of straight carbon fibers through pyrolysis of natural gas at temperatures of 950° - 1075° C., *Appl. Phys. Lett.* 42(8):666(18\983). The fibers are reported to grow in two stages where the fibers first lengthen catalytically
10 and then thicken by pyrolytic deposition of carbon. Tibbetts reports that these stages are "overlapping", and is unable to grow filaments free of pyrolytically deposited carbon. In addition, Tibbett's approach is commercially impracticable for at least two reasons.
15 First, initiation of fiber growth occurs only after slow carbonization of the steel tube (typically about ten hours), leading to a low overall rate of fiber production. Second, the reaction tube is consumed in the fiber forming process, making commercial scale-up
20 difficult and expensive.

In 1983, Tennent, U.S. Patent No. 4,663,230 succeeded in growing cylindrical ordered graphite cores, uncontaminated with pyrolytic carbon, resulting in smaller diameter fibrils, typically 35 to 700 \AA (0.0035
25 to 0.070μ), and an ordered "as grown" graphitic surface. Tennent '230 describes carbon fibrils free of a continuous thermal carbon overcoat and having multiple graphitic outer layers that are substantially parallel to the fibril axis. They may be characterized as having
30 their c-axes, (the axes which are perpendicular to the tangents of the curved layers of graphite) substantially perpendicular to their cylindrical axes, and having diameters no greater than 0.1μ and length to diameter ratios of at least 5.

35 Tennent, et al., US Patent No. 5,171,560 describes carbon fibrils free of thermal overcoat and having graphitic layers substantially parallel to the

fibril axes such that the projection of said layers on said fibril axes extends for a distance of at least two fibril diameters. Typically, such fibrils are substantially cylindrical, graphitic nanotubes of substantially constant diameter and comprise cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis. They are substantially free of pyrolytically deposited carbon, have a diameter less than 0.1μ and a length to diameter ratio of greater than 5.

Moy et al., USSN 07/887,307 filed May 22, 1992, describes fibrils prepared as aggregates having various macroscopic morphologies (as determined by scanning electron microscopy) including morphologies resembling bird nests ("BN"), combed yarn ("CY") or "open net" ("ON") structures.

Multi-walled carbon nanotubes of a morphology similar to the catalytically grown fibrils described above have been grown in a high temperature carbon arc (Iijima, Nature 354 56 1991). (Iijima also describes arc-grown single-walled nanotubes having only a single layer of carbon arranged in the form of a linear Fullerene.) It is now generally accepted (Weaver, Science 265 1994) that these arc-grown nanofibers have the same morphology as the earlier catalytically grown fibrils of Tennent. **Single-walled Carbon Nanotubes**

As mentioned above, the Iijima method partially results in single-walled nanotubes, i.e., nanotubes having only a single layer of carbon arranged in the form of a linear Fullerene.

United States Patent No. 5,424,054 to Bethune et al. describes a process for producing single-walled carbon nanotubes by contacting carbon vapor with cobalt catalyst. The carbon vapor is produced by electric arc heating of solid carbon, which can be amorphous carbon, graphite, activated or decolorizing carbon or mixtures thereof. Other techniques of carbon heating are

discussed, for instance laser heating, electron beam heating and RF induction heating.

Smalley (Guo, T., Nikoleev, P., Thess, A., Colbert, D.T., and Smally, R.E., Chem. Phys. Lett. 243: 1-12 (1995)) describes a method of producing single-walled carbon nanotubes wherein graphite rods and a transition metal are simultaneously vaporized by a high-temperature laser.

Smalley (Thess, A., Lee, R., Nikolaev, P., Dai, H., Petit, P., Robert, J., Xu, C., Lee, Y.H., Kim, S.G., Rinzler, A.G., Colbert, D.T., Scuseria, G.E., Tonárek, D., Fischer, J.E., and Smalley, R.E., Science, 273: 483-487 (1996)) also describes a process for production of single-walled carbon nanotubes in which a graphite rod containing a small amount of transition metal is laser vaporized in an oven at about -1200°C. Single-wall nanotubes were reported to be produced in yields of more than 70%.

Each of the techniques described above employs (1) solid carbon as the carbon feedstock. These techniques are inherently disadvantageous. Specifically, solid carbon vaporization via electric arc or laser apparatus is costly and difficult to operate on the commercial or industrial scale.

Supported metal catalysts for formation of SWNT are also known. Smalley (Dai, H., Rinzler, A.G., Nikolaev, P., Thess, A., Colbert, D.T., and Smalley, R.E., Chem. Phys. Lett. 260: 471-475 (1996)) describes supported Co, Ni and Mo catalysts for growth of both multi-walled nanotubes and single-walled nanotubes from CO, and a proposed mechanism for their formation.

However, supported metal catalysts are inherently disadvantageous, as the support is necessarily incorporated into the single-walled carbon nanotube formed therefrom. Single-walled nanotubes contaminated with the support material are obviously less desirable

compared to single-walled nanotubes not having such contamination.

OBJECTS OF THE INVENTION

5 It is thus an object of the present invention to provide a method of producing single-walled carbon nanotubes which employs a gaseous carbon feedstock.

 It is an object of this invention to provide a method of producing single-walled carbon nanotubes which
10 employs a gas phase, metal containing compound which forms a metal containing catalyst.

 It is also an object of the invention to provide a method of producing single-walled carbon nanotubes which employs an unsupported catalyst.

15 It is a further object of this invention to provide a method of producing single-walled carbon nanotubes which employs a gaseous carbon feedstock and an unsupported gas phase metal containing compound which forms a metal containing catalyst.

20

SUMMARY OF THE INVENTION

 The invention relates to a gas phase reaction in which a gas phase metal containing compound is introduced into a reaction mixture also containing a
25 gaseous carbon source. The carbon source is typically a C₁ through C₆ compound having as hetero atoms H, O, N, S or Cl, optionally mixed with hydrogen. Carbon monoxide or carbon monoxide and hydrogen is a preferred carbon feedstock.

Increased reaction zone temperatures of approximately 400°C to 1300°C and pressures of between -0 and -100 p.s.i.g., are believed to cause decomposition of the gas phase metal containing compound to a metal containing catalyst. Decomposition may be to the atomic metal or to a partially decomposed intermediate species. The metal containing catalysts (1) catalyze CO decomposition and (2) catalyze SWNT formation. Thus, the invention also relates to forming SWNT via catalytic decomposition of a carbon compound.

The invention may in some embodiments employ an aerosol technique in which aerosols of metal containing catalysts are introduced into the reaction mixture. An advantage of an aerosol method for producing SWNT is that it will be possible to produce catalyst particles of uniform size and scale such a method for efficient and continuous commercial or industrial production. The previously discussed electric arc discharge and laser deposition methods cannot economically be scaled up for such commercial or industrial production.

Examples of metal containing compounds useful in the invention include metal carbonyls, metal acetyl acetonates, and other materials which under decomposition conditions can be introduced as a vapor which decomposes to form an unsupported metal catalyst.

Catalytically active metals include Fe, Co, Mn, Ni and Mo. Molybdenum carbonyls and Iron carbonyls are the preferred metal containing compounds which can be

decomposed under reaction conditions to form vapor phase catalyst. Solid forms of these metal carbonyls may be delivered to a pretreatment zone where they are vaporized, thereby becoming the vapor phase precursor of the catalyst.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates a reactor capable of producing SWNT.

Fig. 2 illustrates the vaporizer component of the reactor described in Fig. 1.

DESCRIPTION OF PREFERRED EMBODIMENTS

It has been found that two methods may be employed to form SWNT on unsupported catalysts. The first method is the direct injection of volatile catalyst. The direct injection method is described in copending application Serial No. 08/459,534, incorporated herein by reference.

Direct injection of volatile catalyst precursors has been found to result in the formation of SWNT using molybdenum hexacarbonyl $[\text{Mo}(\text{CO})_6]$ and dicobalt octacarbonyl $[\text{Co}_2(\text{CO})_8]$ catalysts. Both materials are solids at room temperature, but sublime at ambient or near-ambient temperatures -- the molybdenum compound is thermally stable to at least 150° , the cobalt compound sublimes with decomposition "Organic Syntheses via Metal Carbonyls," Vol. 1, I. Wender and P. Pino, eds., Interscience Publishers, New York, 1968, p. 40).

The second method uses a vaporizer to introduce the metal containing compound (Fig. 2).

In one preferred embodiment of the invention, the vaporizer 10, shown at Fig. 2, comprises a quartz thermowell 20 having a seal 24 about 1" from its bottom to form a second compartment. This compartment has two 1/4" holes 26 which are open and exposed to the reactant gases. The catalyst is placed into this compartment, and then vaporized at any desired temperature using a vaporizer furnace 32. This furnace is controlled using a first thermocouple 22.

A metal containing compound, preferably a metal carbonyl, is vaporized at a temperature below its decomposition point, reactant gases CO or CO/H₂ sweep the precursor into the reaction zone 34, which is controlled separately by a reaction zone furnace 38 and second thermocouple 42.

Although applicants do not wish to be limited to a particular theory of operability, it is believed that at the reactor temperature, the metal containing compound is decomposed either partially to an intermediate species or completely to metal atoms. These intermediate species and/or metal atoms coalesce to larger aggregate particles which are the actual catalyst. The particle then grows to the correct size to both catalyze the decomposition of CO and promote SWNT growth. In the apparatus of Fig. 1, the catalyst particles and

the resultant carbon forms are collected on the quartz wool plug 36.

Rate of growth of the particles depends on the concentration of the gas phase metal containing intermediate species. This concentration is determined by the vapor pressure (and therefore the temperature) in the vaporizer. If the concentration is too high, particle growth is too rapid, and structures other than SWNT are grown (e.g., MWNT, amorphous carbon, onions, etc.).

Examples 5 and 6 show many areas of SWNT along with MWNT and other carbon structures. Mo particles ranged from <1-10 nm. In Example 4, mainly MWNT were formed along with other structures of carbon. Mo particles ranged from ~1-50 nm. Presumably, the particles generated in Examples 5 and 6 were the right size to promote SWNT growth over the other forms possible. In Example 4, particle sizes favored growth of MWNT and other forms.

EXAMPLES

Example 1

In a direct injection process, the catalyst compartment was loaded with ~40 mg Molybdenum hexacarbonyl $[\text{Mo}(\text{CO})_6]$ which has been ground to ~100 mesh. The reactor was heated to 900°C under an argon flow. Argon was then replaced with CO at atmospheric pressure at a flow of ~0.8 SLM and the catalyst was injected.

The flow of CO was continued for 30 min. at 900°C, after which it was replaced by argon, and the reactor furnace turned off. After cooling to ambient temperature, the entire contents of the reactor including
5 the quartz wool plug which had been tared prior to the run, was emptied into a tared plastic bag. The quartz wool plug was blackened, but the yield of carbon growth (wgt C/wgt catalyst) was <1.

A specimen for Transmission Electron Microscopy
10 (TEM) was prepared by shaking the quartz wool plug in ethanol in a glass vial and ultrasounding the ethanol for ~2 min. This procedure dispersed the black particles from the quartz wool. A TEM grid was prepared by evaporating several drops of this dispersion onto a
15 carbon-coated copper grid.

Examination of the grid in the TEM showed a mixture of particles and carbon nanotubes, both MW and SW. Particles varied from ~1- several hundred nm and were shown to be Mo by dispersive X-ray analysis. The
20 MWNT ranged from ~4-10 nm diameter. Fishbone fibrils (10-50 nm diameter) were also formed.

Examination of the grid also showed several areas containing SWNT. Diameters ranged between 1-2 nm. TEM estimate of the yield of SWNT was <50% of the carbon
25 formed.

Example 2

The procedure of Ex. 1 was used to produce a mixture of Mo particles and carbon structures including

both MWNT and SWNT. Catalyst charge $[\text{Mo}(\text{CO})_6]$ was ~8 mg. SWNT yield was <50% of all nanotubes produced.

Example 3

The procedure of Example 1 was used to grow
5 SWNT using ~22 mg $\text{Co}_2(\text{CO})_8$ as catalyst. TEM analysis revealed Co particles to be the major component. MWNT and SWNT ranging in diameter from 1-2 nm were also formed. Estimated yield of SWNT was <25% of the nanotubes formed.

10 **Example 4**

A simulated aerosol reactor (Fig. 1) was used to produce SWNT. As the catalyst sublimed in the vaporizer, the vapors were swept by the reactant gases into the reaction section where they underwent immediate
15 thermal decomposition to Mo atoms and CO. It is theorized that the Mo atoms aggregated and promoted growth of carbon structures, including SWNT. These were caught on the quartz wool plug.

Approximately 20 mg of $\text{Mo}(\text{C})_6$ was loaded into
20 the vaporizer. Under argon at atmospheric pressure, the reactor section was heated to 900°C while keeping the vaporizer at ambient temperature. The argon stream was then changed to CO @~0.8 SLM and H_2 @~0.08 SLM, and while maintaining 900° in the reactor, the vaporizer
25 temperature was raised to 70°C. Over the course of the run (1.5 hrs) the vaporizer temperature rose to 80°C due to heat from the reactor furnace. The vapor pressure of $\text{Mo}(\text{CO})_6$ varied from 0.6-10 torr.

TEM specimens were made by the same procedure as Ex. 1. TEM examination showed mainly very small particles of Mo ranging from ~1-10 nm. Also produced were amorphous carbon structures and MWNT with diameters ~4 nm. SWNT with diameters ~1.5 nm were also produced, but in low yield.

Example 5

A procedure similar to Ex. 4 where ~20 mg Mo(CO)_6 was loaded in the vaporizer. With the reactor at atmospheric pressure at 900°C, the vaporizer temperature was set at 40°C and CO was fed to the system @~0.8 SLM. Over the course of the run (1.5 hrs) the vaporizer temperature rose to 57°C. For this temperature span, the vapor pressure of Mo(CO)_6 ranged from 0.6-2 torr.

TEM examination showed mainly Mo nanoparticles 1-10 nm in diameter along with various carbon structures. These included amorphous carbon and MWNT with diameters of 4-10 nm. However, also produced were SWNT with diameters varying from ~1-3 nm. Estimated yield of SWNT was <20% of the nanotubes produced.

Example 6

Using the procedure of Exs. 4-5, ~20 mg Mo(CO)_6 was vaporized at 38-41°C into the reactor zone which was set at 900°C. The feed gas comprised CO @0.8 SLM and H_2 @0.08 SLM and was fed at atmospheric pressure for 2.0 hrs. Vapor pressure of catalyst was nearly constant at ~0.6 torr.

TEM examination showed the presence of Mo nanoparticles, many ~ 1 nm diameter. The usual amorphous carbon and MWNT with diameters ranging from 4-10 nm were seen. However, SWNT, 1-3 nm in diameter were also
5 produced at a yield of ~50% of the nanotubes produced.

Example 7

Examples 1-6 are summarized in Table I.
Precursor was obtained as a powder from ALFA/AESAR, Research Chemicals and Materials. They were ground under
10 an argon blanket to --100 mesh.

5

RUN #	CATALYST PRECURSOR	FEEDSTOCK COMPOSITION	REACTOR TEMP	VAPORIZER TEMP	STEM	SWNT
1*	Mo(CO) ₆	CO-100%	900°C	NA	Mix of particles and MWNT/SWNT	<50%
2*	Mo(CO) ₆	CO-100%	900°C	NA	Same as above; X-ray showed no Fe	<50%
3*	Co ₂ (CO) ₈	CO-100%	900°C	NA	Mostly particles, some SWNT strings	<25%
4**	Mo(CO) ₆	CO-90% H ₂ -10%	900°C	70-80°C	Mostly particles, MWNT	trace
5**	Mo(CO) ₆	CO-100%	900°C	40-57°C	Mostly particles and MWNT, some SWNT	<20%
6**	Mo(CO) ₆	CO-90% H ₂ -10%	900°C	38-41°C	Particles, few MWNT, more SWNT	~50%

10

* Direct Injection Method
 **Simulated Aerosol Method

Example 8

15 Ferrocene (C₅H₅)₂Fe is substituted for the molybdenum hexacarbonyl in the procedure of Example 2 at an appropriate vapor pressure and temperature.

Examination of the grid in the TEM shows a mixture of particles and carbon nanotubes, both MW and SW. Particles vary from ~1- several hundred nm. The
 20 MWNT ranges from ~4-10 nm diameter.

Examination of the grid also shows several areas containing SWNT. Diameters range between 1-2 nm. TEM estimate of the yield of SWNT was <50% of the carbon formed.

Example 9

Ferrocene (C_5H_5)₂Fe is substituted for the molybdenum hexacarbonyl in the procedure of Example 6 at an appropriate vapor pressure and temperature.

Examination of the grid in the TEM shows a mixture of particles and carbon nanotubes, both MW and SW. Particles vary from ~1- several hundred nm. The MWNT ranges from ~4-10 nm diameter.

Examination of the grid also shows several areas containing SWNT. Diameters range between 1-2 nm. TEM estimate of the yield of SWNT was <50% of the carbon formed.

Example 10

Methylcyclopentadienyl manganese tricarbonyl ($CH_3C_5H_4$)Mn(CO)₃ is substituted for the molybdenum hexacarbonyl in the procedure of Example 2 at an appropriate vapor pressure and temperature.

Examination of the grid in the TEM shows a mixture of particles and carbon nanotubes, both MW and SW. Particles vary from ~1- several hundred nm. The MWNT ranges from ~4-10 nm diameter.

Examination of the grid also shows several areas containing SWNT. Diameters range between 1-2 nm. TEM estimate of the yield of SWNT was <50% of the carbon formed.

Example 11

Methylcyclopentadienyl manganese tricarbonyl ($\text{CH}_3\text{C}_5\text{H}_4$)Mn(CO)₃ is substituted for the molybdenum hexacarbonyl in the procedure of Example 6 at an appropriate vapor pressure and temperature.

Examination of the grid in the TEM shows a mixture of particles and carbon nanotubes, both MW and SW. Particles vary from ~1- several hundred nm. The MWNT ranges from ~4-10 nm diameter.

Examination of the grid also shows several areas containing SWNT. Diameters range between 1-2 nm. TEM estimate of the yield of SWNT was <50% of the carbon formed.

Example 12

Cyclopentadienyl cobalt dicarbonyl (C_5H_5)Co(CO)₂ is substituted for the molybdenum hexacarbonyl in the procedure of Example 2 at an appropriate vapor pressure and temperature.

Examination of the grid in the TEM shows a mixture of particles and carbon nanotubes, both MW and SW. Particles vary from ~1- several hundred nm. The MWNT ranges from ~4-10 nm diameter.

Examination of the grid also shows several areas containing SWNT. Diameters range between 1-2 nm. TEM estimate of the yield of SWNT was <50% of the carbon formed.

Example 13

Cyclopentadienyl cobalt dicarbonyl (C_5H_5)Co(CO) $_2$ is substituted for the molybdenum hexacarbonyl in the procedure of Example 6 at an appropriate vapor pressure and temperature.

Examination of the grid in the TEM shows a mixture of particles and carbon nanotubes, both MW and SW. Particles vary from ~1- several hundred nm. The MWNT ranges from ~4-10 nm diameter.

Examination of the grid also shows several areas containing SWNT. Diameters range between 1-2 nm. TEM estimate of the yield of SWNT was <50% of the carbon formed.

Example 14

Nickel dimethylglyoxime ($HC_4H_6N_2O_2$)Ni is substituted for the molybdenum hexacarbonyl in the procedure of Example 2 at an appropriate vapor pressure and temperature.

Examination of the grid in the TEM shows a mixture of particles and carbon nanotubes, both MW and SW. Particles vary from ~1- several hundred nm. The MWNT ranges from ~4-10 nm diameter.

Examination of the grid also shows several areas containing SWNT. Diameters range between 1-2 nm. TEM estimate of the yield of SWNT was <50% of the carbon formed.

Example 15

Nickel dimethylglyoxime ($\text{HC}_4\text{H}_6\text{N}_2\text{O}_2$)Ni is substituted for the molybdenum hexacarbonyl in the procedure of Example 6 at an appropriate vapor pressure and temperature.

- 5 Examination of the grid in the TEM shows a mixture of particles and carbon nanotubes, both MW and SW. Particles vary from ~1- several hundred nm. The MWNT ranges from ~4-10 nm diameter.

- Examination of the grid also shows several
10 areas containing SWNT. Diameters range between 1-2 nm. TEM estimate of the yield of SWNT was <50% of the carbon formed.

CLAIMS:

1. A process for producing hollow, single-walled carbon nanotubes by catalytic decomposition of one or more gaseous carbon compounds comprising the steps of:

5 (1) forming a gas phase mixture of

(a) a carbon feed stock gas comprising one or more gaseous carbon compounds, each said compound having one to six carbon atoms and only H, O, N, S or Cl as hetero atoms, optionally admixed with hydrogen, and

10 (b) a gas phase metal containing compound which is unstable under reaction conditions for said decomposition, and which forms a metal containing catalyst which acts as a decomposition catalyst under reaction conditions;

15 (2) conducting said decomposition reaction under decomposition reaction conditions and thereby producing said nanotubes.

2. The method defined in claim 1, wherein 50% or more of said carbon feedstock gas is carbon monoxide.

20 3. The method defined in claim 1, wherein said carbon feedstock gas consists essentially of carbon monoxide.

4. The method defined in claim 1, wherein said decomposition reaction occurs at temperatures
25 between approximately 400°C and approximately 1300°C.

5. The method defined in claim 1, wherein said decomposition reaction occurs at temperatures between approximately 700°C and approximately 1100°C.

6. The method defined in claim 1, wherein said decomposition reaction occurs at a pressure range of approaching 0 p.s.i.g. through approximately 100 p.s.i.g.

7. The method defined in claim 1, wherein
5 said gas phase metal containing compound is produced by vaporizing a liquid or solid phase metal containing compound.

8. The method defined in claim 7, wherein said metal containing compound is vaporized into a
10 flowing stream of carbon feedstock, wherein the temperature of said flowing stream is between approximately 400°C and approximately 1300°C and wherein said flowing stream is at a pressure range of approaching 0 p.s.i.g. through approximately 100 p.s.i.g.

15 9. The method defined in claim 1, wherein said gas phase metal containing compound is mixed with said feedstock by direct injection.

10 10. The method defined in claim 1, wherein said gas phase metal containing compound is in the form of an aerosol.

11. The method defined in claim 1, wherein said gas phase metal containing compound is $\text{Mo}(\text{CO})_6$.

12. The method defined in claim 1, wherein said gas phase metal containing compound is $\text{Co}_2(\text{CO})_8$.

25 13. The method defined in claim 1, wherein said gas phase metal containing compound is a volatile iron compound.

14. The method of claim 13, wherein said volatile iron compound is ferrocene.

15. The method defined in claim 1, wherein said gas phase metal containing compound is a volatile manganese compound.

16. The method of claim 15, wherein said volatile manganese compound is methylcyclopentadienyl manganese tricarbonyl.

17. The method defined in claim 1, wherein said gas phase metal containing compound is a volatile cobalt compound.

18. The method of claim 17, wherein said volatile cobalt compound is cyclopentadienyl cobalt dicarbonyl.

19. The method defined in claim 1, wherein said gas phase metal containing compound is a volatile nickel compound.

20. The method of claim 19, wherein said volatile nickel compound is nickel dimethylglyoxime.

21. The method defined in claim 1, wherein said gas phase metal containing compound is produced by subliming a solid phase metal containing compound.

22. The method defined in claim 1, wherein said gas phase metal containing compound is produced by vaporizing a liquid phase metal containing compound.

23. Single-walled carbon nanotubes produced by catalytic decomposition of one or more gaseous carbon compounds comprising the steps of:

(1) forming a gas phase mixture of

(a) a carbon feed stock gas comprising one or more gaseous carbon compounds, each having one to six carbon atoms and only H, O, N, S or Cl as hetero atoms, optionally admixed with hydrogen, and

(b) a gas phase metal containing compound which is unstable under reaction conditions for said decomposition, and which forms a metal containing catalyst which acts as a decomposition catalyst under reaction conditions;

(2) conducting said decomposition reaction under decomposition reaction conditions and thereby producing said nanotubes.

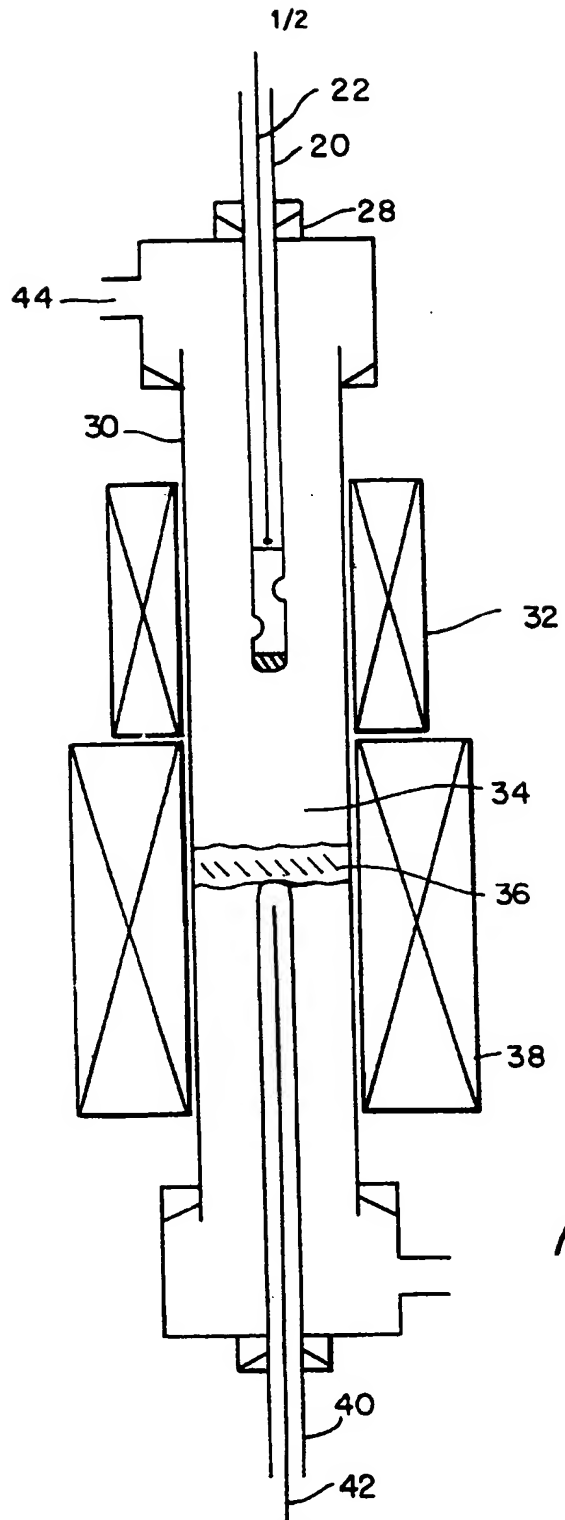


FIG. 1

2/2

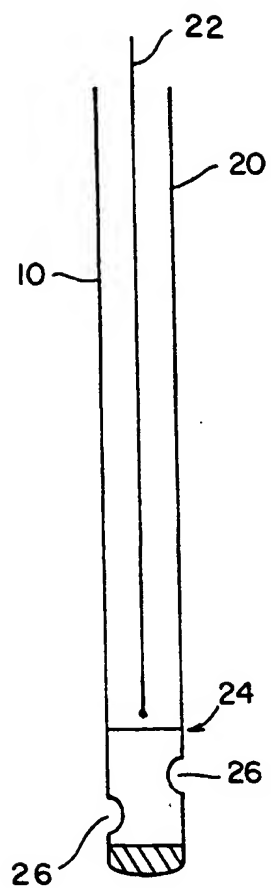


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/16071

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : D01F 9/12, 9/127; C01B 31/02

US CL : 423/445B, 447.2, 447.3

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/445B, 447.2, 447.3

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,374,415 A (ALIG, et al.) 20 December 1994, column 5, line 15- column 6, line 22 and column 2, lines 47-65.	1, 4-7, 9, 13, and 22
X	JP 09-188,509 A (YOSHIKAWA) 22 July 1997, see entire document.	1, 4-5, 7-9, 13-14 and 21
Y	JP 06-322,615 A (IJIJIMA et al.) 22 November 1994, see entire document.	1-22
Y	GB 2,248,230 A (KAWAGUCHI et al.) 04 January 1992, see page 4, lines 7-25 and page 7, lines 17-26 and page 8, lines 1-3.	1-22
X	KIANG, C-H. Carbon Nanotubes with Single-layer Walls. Carbon. August 1995, see page 903.	23



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

19 OCTOBER 1998

Date of mailing of the international search report

19 NOV 1998

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

MICHAEL LEWIS

Telephone No. (703) 368-0680

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☒ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.